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Title: Method for the Purification of Terephthalic Acid

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Patent Application

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1. Title of the Invention

Method for the Purification of Terephthalic Acid

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SPECIFICATION

1. Title of the Invention

Method for the Purification of Terephthalic Acid

2. Claims

A method for the purification of terephthalic acid, characterized in that crude terephthalic acid obtained as a result of oxidizing p-dialkyl benzene with a gas containing molecular oxygen is heated in a suspended state in a glycol or a solution whose principal components is a glycol in an amount 0.35 to 10 times the weight of the crude terephthalic acid from 60°C up to the boiling point of the glycol used, after which the terephthalic acid and the glycol are separated.

3. Detailed Description of the Invention

The present invention relates to a method in which crude terephthalic acid obtained as a result of oxidizing p-dialkyl benzene is purified to yield a terephthalic acid of a good, consistent quality.

Crude terephthalic acid that is obtained on a commercial scale generally contains minute amounts of colored impurities. In order for the acid to be used as a raw material for polyester fibers, it is necessary to remove these impurities and to purify the terephthalic acid. The impurities in crude terephthalic acid differ greatly depending on the manufacturing lot. When they are used in unaltered form in the manufacture of polyesters, polyesters of consistent quality cannot be obtained. Therefore, the terephthalic acid must be purified so that the quantity of impurities remains constant.

In particular, crude terephthalic acid that is manufactured as a result of oxidizing p-xylene in the liquid phase with the help of a gas containing molecular oxygen (air in commercial conditions) using a lower monocarboxylic acid as the solvent and a heavy metal salt such as cobalt, manganese, nickel or chromium as the catalyst, preferably in the presence of a halogen such as bromine as a promoter, contains organic impurities such as 4-carboxybenzaldehyde (hereafter, 4-carboxybenzaldehyde is abbreviated as 4-CBA), the catalyst metals, and halogens, as well as the titanium and iron admixed as the result of corrosion of the

manufacturing apparatus. Of these, 4-CBA has a marked effect on coloration, and the amount of 4-CBA must be minimized and kept at a constant level.

Several methods have so far been proposed for the purpose of removing these impurities. For example, there is a method in which crude terephthalic acid (hereafter terephthalic acid is abbreviated as TA) is dissolved at a high temperature and pressure in water or an organic solvent, and the product is crystallized; a method in which an aqueous solution of an alkali salt is formed, and the product is precipitated with an acid; and a method in which these treatments include chemical treatments such as oxidation and reduction, as well as ion exchange treatments.

Although high-purity TA can be obtained as a result of these methods, considerable expense is necessary for the purification treatments, resulting in a more expensive product. When high temperature and high pressure are used in these methods, special reaction equipment is necessary and there is the danger that some of the TA will be decomposed or that there will be coloration because of secondary reactions. Further, in treatments involving alkali salt dissolution, oxidation, reduction, and adsorption, there are the drawbacks that expensive chemical products must be used and that processes and operations are complex.

The inventors conducted various studies of TA purification methods which could be implemented industrially and which would be economical. As the result, they discovered that purified TA can be manufactured easily by means of heating crude TA in a suspended state in a glycol or a solution whose principal component is a glycol in an amount 0.4 to 10 times the TA weight from 60°C up to the boiling point of the glycol used, after which the TA and the glycol are separated, and that polyethylene terephthalate fibers of excellent whiteness can be obtained using this TA.

Further, although the quality of crude TA differs greatly depending on the manufacturing lot, the quality of the purified TA can be made consistent by means of taking the quality of crude TA into account and appropriately adjusting the conditions under which the TA is heated in the glycol. Consequently, polyethylene terephthalate fibers that are of good, consistent quality can be obtained.

As a result of this invention, TA is purified at or below the boiling point of glycol, the treatment can be performed at normal pressure, and special equipment is not necessary. Moreover, the objective can be reached in a short time of several minutes to several tens of minutes, and a high-volume treatment can be conducted in a low-capacity apparatus. In addition, the chemical agent used is an inexpensive glycol. In particular, when ethylene glycol (hereafter, ethylene glycol is abbreviated as EG) is used, the EG can be used as a raw material in the manufacture of the polyethylene terephthalate, and it is thus not necessary to separate the EG. In addition, the process of drying the purified TA can be omitted. Consequently, the present invention is characterized by low equipment and operating costs.

The content of impurities such as 4-CBA in the TA that is obtained as a result of this invention is greatly reduced. Attention should be drawn to the fact that impurities are removed and that a polyesters of superior whiteness can be obtained by means of the simple purification procedure of this invention.

The crude TA that is purified as a result of the method of the present invention is obtained in response to oxidizing p-dialkyl benzenes such as, for example, p-xylene, p-ethyl toluene, and p-diisopropylbenzene by means of a gas containing molecular oxygen. For example, it is possible to use a crude terephthalic acid obtained as a result of the methods described in the specifications of JP (Kokoku) 34-2666, JP (Kokoku) 35-4963, and U.S. Patent No. 3139452, and, in particular, by means of oxidizing p-xylene using a cobalt and/or manganese catalyst and employing a lower aliphatic carboxylic acid such as acetic acid or propionic acid as the solvent.

Further, the glycols that are used in this invention include EG, propylene glycol, 1,2-butanediol, trimethylene glycol and tetramethylene glycol, with EG being particularly desirable.

The quantity of glycol should be 0.35 to 10 times the weight of crude TA, with 0.5 to 5 times the TA weight being particularly desirable. When the quantity is less than 0.35 times, the effect is not obtained. In addition, the fluidity of the suspension, which is in the form of a slurry, is reduced and the suspension is difficult to handle. When more than 10 times the weight is used,

the effect is not particularly increased and a larger treatment apparatus is needed. This is not desirable.

TA forms a so-called slurried state if the quantity of suspended glycol is small. When treatment is performed at a high temperature for a long time, some TA is dissolved in glycol. However, when conditions that are ordinarily used are adopted in this invention, there is essentially no dissolution of the TA in the glycol, and solely the impurities contained in the crude TA are dissolved into the glycol.

The treatment temperature in this invention should be from 60°C up to the boiling point of the glycol that is used, with a temperature from 80°C up to the boiling point of the glycol being particularly desirable. At less than 60°C, there is no effect, and above the boiling point of the glycol, the pressure of the treatment system is increased, special equipment is necessary, and some of the TA readily dissolves in the glycol. This is not desirable.

Such treatments as centrifugation, filtration, and drying by means of standard methods can be performed to separate the glycol in the TA that has undergone the heat treatment in the glycol according to this invention. When a glycol that is the same as the glycol used in the treatment is used, it is not necessary to completely separate the purified TA and the glycol, and a TA to which some of the glycol is still attached can be directly used in the manufacture of polyesters.

Next, we shall present a specific explanation of the present invention by means of working examples. In the working examples, the content of 4-CBA in the TA was determined quantitatively with the help of polarography and was expressed as percent by weight relative to the crude TA or purified TA.

Polymer whiteness is a value found as a result of dissolving 0.333 g of polyester manufactured using TA as the raw material in 10 mL of a mixed solution of equal quantities of phenol and tetrachloroethane, introducing the solution into a 3 cm cell, measuring transmittance at 410 and 550 mμ (T_{410} , T_{550} : %), and calculating whiteness by the following equation.

$$\text{Polymer whiteness } W_{410} = 4T_{410} - 3T_{550} \quad (\%)$$

Polyester was manufactured under the following conditions. 86 parts ("parts" indicates a quantity based on weight in all cases) of terephthalic acid, 96 parts of ethylene glycol and 0.04 parts of sodium hydrogen phosphate (-) were introduced into an autoclave equipped with a distillation column, and a reaction was carried out at a temperature of 240°C and a pressure of 2.2 kg/cm² (gauge) as gas was being extracted with the help of gas extraction. Distilling out of water was stopped, after which the pressure was reduced to 1.0 kg/cm² (gauge), and the reaction was carried out for another 20 minutes. 0.03 parts of antimony was added to the reaction product, and the temperature was raised to 260°C over a period of 30 minutes. Next, the temperature was raised to 295°C, requiring 30 minutes as the pressure was gradually reduced to 760 mmHg. Following that, a condensation reaction was carried out for 110 minutes at a temperature of 295°C and a pressure of 1 mmHg or lower. After polymerization had been completed, polyethylene terephthalate fibers that had been extruded from the spinneret installed in the bottom part of the polymerization vessel were obtained.

The $[\eta]$ value of the polymer is the limiting viscosity measured at 30° as a result of dissolving the polyester that has been obtained in a mixed solvent of equal quantities of phenol and tetrafluoroethane.

Table 1 summarizes the results of the working examples and comparative examples.

Working Example 1

Crude TA containing 0.40% of 4-CBA was heated for 7 minutes at 100°C in 1.4 times the EG weight as the materials were being stirred, after which centrifugation was performed and the TA and EG were separated. The quantity of 4-CBA in the TA that was obtained was 0.32%. The $[\eta]$ value of the polyester obtained using this TA was 0.66, and its whiteness was 18%.

Comparative Example 1

When the crude TA used in Working Example 1 was directly used for polymerization without performing the treatment of this invention, the $[\eta]$ value of the resulting polyester was 0.65, and its whiteness was -4%.

Working Examples 2 to 9

The crude TA used in Working Example 1 and Comparative Example 1 was subjected to a heat treatment in EG under various conditions according to this invention. Brief treatments resulted in a reduction in the quantity 4-CBA and enhanced polymer whiteness. A tendency was found for the purifying effect to increase as the treatment temperature was raised.

Working Examples 10 to 27 and Comparative Examples 2 and 3

Table 1. Results of Purification and Polymerization of Crude TA (E indicates working examples and C indicates comparative examples)

No.	4-CBA in crude TA (%)	Glycol		Purification treatment conditions		4-CBA in purified CBA (%)	Polyester	
		Type	Times weight of crude TA	Temperature (°C)	Time (minutes)		[η] (dL/g)	Whiteness (%)
C-1	0.40	(no	treatment)	-	-	-	0.65	4
E-1	0.40	EG	1.4	100	7	0.32	0.66	18
E-2	0.40	EG	1.4	100	20	0.27	0.65	23
E-3	0.40	EG	1.4	100	40	0.26	0.66	24
E-4	0.40	EG	1.4	150	7	0.25	0.65	30
E-5	0.40	EG	1.4	150	20	0.21	0.67	36
E-6	0.40	EG	1.4	150	40	0.21	0.67	37
E-7	0.40	EG	1.4	190	7	0.21	0.67	35
E-8	0.40	EG	1.4	190	20	0.18	0.67	41
E-9	0.40	EG	1.4	190	40	0.18	0.68	42
C-2	0.24	(no	treatment)	-	-	-	0.67	13
E-10	0.24	EG	1.4	100	7	0.18	-	-
E-11	0.24	EG	1.4	100	20	0.17	-	-
E-12	0.24	EG	1.4	100	40	0.14	0.68	46
E-13	0.24	EG	1.4	150	7	0.14	-	-
E-14	0.24	EG	1.4	150	20	0.12	-	-
E-15	0.24	EG	1.4	150	40	0.12	0.69	50
E-16	0.24	EG	1.4	190	7	0.12	0.69	52
E-17	0.24	EG	1.4	190	20	0.10	-	-
E-18	0.24	EG	1.4	190	40	0.10	0.69	56

No.	4-CBA in crude TA (%)	Glycol		Purification treatment conditions		4-CBA in purified CBA (%)	Polyester	
		Type	Times weight of crude TA	Temperature (°C)	Time (minutes)		[η] (dL/g)	Whiteness (%)
C-3	0.15	(no	treatment)	-	-	-	0.67	27
E-19	0.15	EG	1.4	100	7	0.12	0.68	53
E-20	0.15	EG	1.4	100	20	0.11	-	-
E-21	0.15	EG	1.4	100	40	0.10	0.69	56
E-22	0.15	EG	1.4	150	7	0.08	0.69	57
E-23	0.15	EG	1.4	150	20	0.08	-	-
E-24	0.15	EG	1.4	150	40	0.07	0.70	60
E-25	0.15	EG	1.4	190	7	0.08	0.69	59
E-26	0.15	EG	1.4	190	20	0.06	0.70	63
E-27	0.15	EG	1.4	190	40	0.06	0.69	63
C-4	0.27	(no	treatment)	-	-	-	0.67	10
C-5	0.27	EG	0.5	190	15	0.23	0.67	18
E-28	0.27	EG	0.6	190	15	0.11	0.68	55
E-29	0.27	EG	2.0	190	15	0.10	0.68	54
E-30	0.27	EG	4.0	190	15	0.11	0.69	54
E-31	0.27	Propylene glycol	1.4	150	15	0.13	0.68	51
E-32	0.27	Tetra- methylene glycol	1.4	150	15	0.12	0.68	50

A heat treatment was performed in EG under various conditions according to this invention by means of using crude TA containing 0.24% and 0.15% 4-CBA. Similar to Working Examples 1 to 9, the results that were obtained were a reduction in the quantity of 4-CBA and an increase in polymer whiteness as a result of a brief treatment. Further, the purifying effect increased with increased treatment temperature.

Working Examples 28 to 30 and Comparative Examples 4 and 5

Crude TA containing 0.27% 4-CBA was used, the amount of EG was varied, and a purification treatment was performed. In Working Examples 28 to 30, a considerable purifying effect was achieved, whereas in Comparative Example 4 essentially no purification effect was found. In Comparative Example 5, the interior of the system could not be stirred uniformly.

Working Examples 31 and 32

Purification treatment was performed using propylene glycol and tetramethylene glycol as the glycols. As with EG, the amount of 4-CBA was reduced and a polymer of superior whiteness was obtained.

5. List of Attached Documents

- | | |
|-----------------------|--------|
| (1) Duplicate | 1 copy |
| (2) Specification | 1 copy |
| (3) Power of Attorney | 1 copy |



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JAPANESE / ENGLISH TRANSLATION OF

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15 Commissioner, Patent Office: Mr. Takehisa INOUE

1. Title of the Invention

Method for Refining Crude Terephthalic Acid

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5. Attachments

(1) Specification 1 copy
(2) Copy of application 1 copy
(3) Power of Attorney 1 copy
Formal Examination (Ishikawa)
46 059004

SPECIFICATION

1. Title of the Invention

Method for Refining Crude Terephthalic Acid

2. Claims

5 A method for refining crude terephthalic acid characterized in that crude terephthalic acid is treated for 3 to 60 min at a temperature of 160 to 300°C in the presence of a diol having a boiling point within a range of 160 to 300°C, and in a state where at least a portion of the terephthalic acid is present in the form of a solid, whereupon the terephthalic acid is fractionated.

3. Detailed Description of the Invention

10 (Field of Industrial Utilization)

 The present invention relates to a method for refining crude terephthalic acid, and in particular relates to a method for manufacturing high-purity terephthalic acid that may be used in a so-called direct process, wherein a reaction is brought about with ethylene glycol or ethylene oxide directly, and, in particular, without involving a dialkyl ester, to induce polymerization and
15 to yield polyethylene terephthalate.

 A variety of acid treatments, reduction treatments, recrystallization treatments, and sublimation treatments, as well as combinations of such treatments are among numerous methods that have been proposed for increasing the purity of crude terephthalic acid. Other methods include so-called "slurry treatments," wherein a treatment is performed while the crude
20 terephthalic acid is suspended in a variety of solvents. The simplest is one in which rinsing is performed in slurried state, that is, a slurry rinsing process is carried out.

 Air oxidation of paraxylene is a typical method used to manufacture terephthalic acid. A variety of impurities are contained within crude terephthalic acid obtained by means of air oxidation, with those presenting the greatest problems being di-substituted aromatic aldehydes and coloring impurities. Crude terephthalic acid that contains such impurities will not yield so-called "fiber-grade" polyethylene terephthalate, even if reacted with ethylene glycol or ethylene
25 oxide. Methods used hitherto for refining terephthalic acid that can yield fiber-grade

polyethylene terephthalate have involved completely dissolving the terephthalic acid in a suitable solvent, and performing a reduction treatment or an oxidation treatment in solution.

5 In fact, there are no good solvents that can be employed with terephthalic acid; therefore, the terephthalic acid is often either formed into an alkali solution, or treated as a solution under a high temperature and high pressure. In the case of the former, a complicated procedure is required to recover the alkali, while in the latter case the equipment employed therefor creates clear economic disadvantages.

10 Despite several proposals put forth for improving the slurry rinsing methods described above, slurry rinsing continues to be positioned as nothing more than a preliminary pre-treatment for obtaining high-purity terephthalic acid from crude terephthalic acid.

If it were possible to use slurry rinsing merely to obtain roughly the same degree of effect as obtained with the above-described treatments in solution, then economic advantages would be evident; e.g., the amount of solvent could be reduced, the alkali could be obviated, and the high temperatures and pressures could also be dispensed with.

15 It is an object of the present invention to provide a method for refining crude terephthalic acid inexpensively and on an industrial scale.

It is a further object of the present invention to provide an improvement to slurry rinsing methods in order to render crude terephthalic acid into high-purity terephthalic acid that is ideally used in the direct polymerization of polyesters.

20 According to investigations carried out by the present inventors, and in contrast to the commonly prevailing view that scant progress has been made with regard to the use of slurry rinsing for refining high-purity terephthalic acid to the extent achieved with dissolution treatments, the aforementioned objects of the present invention were adjudged to be unexpectedly achievable to a satisfactory degree as a result of using a specific solvent and performing a treatment under specific conditions.

25 The present invention relates to a method for refining crude terephthalic acid characterized in that crude terephthalic acid is treated for 3 to 60 min at a temperature of 160 to

300°C in the presence of a diol having a boiling point within a range of 160 to 300°C, and in a state where at least a portion of the terephthalic acid is present in the form of a solid, whereupon the terephthalic acid is fractionated.

5 According to the present invention, it is possible to remove di-substituted aromatic aldehyde and coloring impurities to a degree hitherto considered unachievable with conventional slurry rinsing.

Specific examples of diols used in the present invention include ethylene glycol (boiling point: 198°C), diethylene glycol (boiling point: 245°C), triethylene glycol (boiling point: 285°C), trimethylene glycol (boiling point: 214°C), propylene glycol (boiling point: 188°C), 1,4-butane-
10 diol (boiling point: 235°C), 1,3-butanediol (boiling point: 208°C), 1,2-butanediol (boiling point: 192 to 194°C), 2,3-butanediol (pinacol) (boiling point: 171 to 172°C), of which ethylene glycol is ideal. The anticipated objectives were surprisingly impossible to achieve when using methyl alcohol, ethyl alcohol, and other monohydric alcohols; or glycerine and other trihydric alcohols.

15 An effect of the type obtained with the present invention cannot be demonstrated when acetic acid,¹ which is a typical solvent for terephthalic acid, is used for rinsing.

In the procedure according to the present invention, part of the terephthalic acid is caused to react with the above diols, and the terephthalic acid is partially dissolved in the mother liquor by means of a partial esterification. However, the conditions may be selected so that the amount of terephthalic acid dissolved as a result of esterification is 5% or less per treatment cycle.

20 The amount is preferably 4% or less, and more preferably 3% or less. In an expanded sense of the means of the present method, any desired esterification preventer or suppressor; e.g., a negative catalyst for use in esterification, is jointly used to prevent esterification.

The treatment is performed at a temperature of 160 to 300°C. It is not desirable for the temperature to be less than 160°C, since the anticipated effect will be impossible to obtain,
25 although a slurry will be produced; nor is it desirable for the temperature to be greater than 300°C because, inter alia, the esterification of the terephthalic acid and diol will accelerate, and

considerable pressure may be required depending on the type of diol used. The optimal range of the treatment temperature will differ according to the type of diol used. A temperature range of 160 to 190°C is especially preferred when ethylene glycol is used.

5 The treatment time is dependent on the treatment temperature, but is commonly 3 to 60 min, preferably 3 to 45 min, and more preferably 5 to 30 min. It is not desirable for the time to be less than three minutes since the anticipated refining effect will be impossible to obtain; nor is it desirable for the time to be greater than 60 min, since the effect will reach a level of saturation, and esterification between the terephthalic acid and diol will become pronounced.

10 A fundamental characteristic of the present invention is that within a specific temperature range the use of a specific diol will enable the effect to be obtained in an extremely short period of time that can be measured in units of "minutes"; and that if the treatment lasts for hours, the resulting effect will instead be undesirable. It is universally known that heating is used to bring about a reaction between terephthalic acid and ethylene glycol or another diol in polymer manufacturing methods. However, such heating is performed in units of "hours", and thus it was
15 entirely unexpected that the terephthalic acid could be refined to a level of high purity as a result of being separated after having been subjected to a heat treatment performed on the order of "minutes."

The treatment of the present invention is preferably performed so as to minimize any loss of terephthalic acid produced as a result of the esterification between the terephthalic acid and
20 diol. For instance, if the rinsing procedure is performed for 5 to 30 min at a temperature of 160 to 190°C with ethylene glycol being used as the diol, the loss of terephthalic acid resulting from esterification can be kept to approximately 3% or less of the amount of introduced terephthalic acid. *Bis*(β -hydroxyethyl)terephthalate (BHT) will be obtained as a result of esterification only when ethylene glycol is used as a diol; therefore, when terephthalic acid has been subjected to
25 the rinsing treatment and is subsequently used as a raw material for polymerizing polyethylene terephthalate, no anomalous circumstances will arise due to the co-presence of the BHT, and the production of BHT during the rinsing procedure should accordingly not cause any great concern. Nevertheless, the loss of BHT in the mother liquor does indeed become a problem in such

¹ [Translator's note: Presumed translation of illegible acid name.]

instances, and a typically recommended process to minimize its occurrence is to keep the filtration temperature as low as possible when fractionating the terephthalic acid after rinsing. All the same, the filtration temperature is associated both with the amount of impurities in the crude terephthalic acid and with the effect related to the removal thereof. It is accordingly most
5 definitely not the case that merely lowering the temperature will be sufficient, but rather that such a decision should be made after having considered the relevant economic ramifications; i.e., whether it is advantageous to reduce the filtration temperature by means of repeatedly performing the treatment of the present invention, or to reduce the number of cycles and raise the filtration temperature.

10 The present invention shall be described in further detail below.

First, crude terephthalic acid having the characteristics described in the foregoing is introduced into a diol having the characteristics described in the foregoing. 4-Carboxybenz-
aldehyde (i.e., "4-CBA") is a typical di-substituted aromatic aldehyde. As used herein, the term
"coloring impurity" refers to a substance that will cause the polyethylene terephthalate polymer
15 obtained from terephthalic acid and ethylene glycol to turn an undesirable color.

The diol used in the present invention preferably has a moisture content of 5% or less so as to yield the dramatic refining effect expected of the present invention. The moisture content is more preferably 3% or less. During the treatment steps described in detail below, a certain
amount of water will be produced² in the system in the present invention as a matter of course,
20 and the moisture content in the diol will gradually increase as a result.² It is accordingly preferable to use a diol having as low a moisture content as possible during the actual procedure.

The resulting blended solution is subsequently heated to the temperature described in the foregoing. Heating may be suitably achieved, for example, as a result of charging the terephthalic acid into a preheated diol, or passing the heated diol through, e.g., a column filled
25 with terephthalic acid (preferably heated to a predetermined temperature). The system to be treated is preferably kept at a normal level of pressure, but exactly the same effect will be obtained using a pressurized system.

² [Translator's note: See Item 6(1) of the Amendment section in the original Japanese text.]

Higher treatment temperatures will reduce the time required for the treatment, but there will be an attendant increase in the ratio of terephthalic acid esterified by the diol; i.e., the amount thereof dissolved in the diol; therefore, the temperature is preferably no higher than 300°C.

5 Esterification begins to progress rapidly from approximately 190°C; therefore, it is especially preferable for the upper limit temperature to be 190°C. At low temperatures, on the other hand, there is a deterioration in the 4-CBA-removing effect, and especially in the refining effect. The treatment temperature is accordingly 160 to 300°C, and especially preferably 165 to 190°C, because the procedure may be performed at normal pressure, and the amount of solute in
10 the diol as a result of esterification or the like may be reduced. The temperature is more preferably 170 to 185°C.

Esterification will tend to be facilitated if the diol is used in an amount of greater than 1000 (weight) parts per 100 parts dry terephthalic acid, while if used in an amount of less than 175 parts, the refining effect will deteriorate, and the treatment operation will be harder to
15 perform. Consequently, the diol is commonly used in an amount of 175 to 1000 parts. An amount of 200 to 800 parts is especially preferred.

The terephthalic acid is subsequently separated in a concentrated form from the mixed solution obtained as a result of the heat treatment described in the foregoing. In one specific example, the resulting solution is filtered. The fractionated terephthalic acid will retain the diol
20 and a small quantity of water. In a further specific example, the diol is charged into the previously described column that has been filled with terephthalic acid particles, and removed from the bottom of the column. In either of these circumstances, it is preferable for the fractionated terephthalic acid particles and mother liquor components held between the particles to be removed as thoroughly as possible, and for the terephthalic acid to be fractionated in a
25 concentrated form whenever possible. In achieving these objectives, it is advantageous for a low-viscosity diol to be used, and preferable for the fractionated terephthalic acid to be further rinsed with acetone, methanol, water, or another low-boiling solvent.

It is, however, undesirable to use such alternate solvents when these steps are repeated. Ideally, and whenever possible, fresh diol is used to replace the mother liquor retained between particles, and to perform rinsing.

When employed as a raw material for use in producing polyethylene terephthalate polymers, the terephthalic acid obtained according to the present invention may be directly
5 subjected to polymerization without the need to remove the ethylene glycol by means of drying, provided that ethylene glycol is used in the treatment of the present invention. The drying equipment ordinarily required therefor is accordingly rendered extraneous, enabling the steps to be streamlined and costs reduced. Consequently, not only will the refining effect be obtained, but
10 also an additional advantage will be gained when ethylene glycol is employed.³

The mother rinse liquor will contain terephthalic acid along with mono- and di-esters thereof in accordance with the solubility at the filtration temperature.

An appropriate treatment may be performed in order to be able to recover these substances, but the filtration temperature may be lowered in order to reduce the amount of
15 substances recovered, depending on the objective of application. In other words, it is preferable to set the lower limit of the filtration temperature to a level equal to or higher than the saturation solubility of the impurities to be removed. Nevertheless, when a large quantity of impurities is present, and all are to be removed with one cycle of treatment, the amount of recoverable substances will also tend to increase as a matter of course, in which case it is advantageous to
20 increase the number of treatment cycles. The filtration temperature is commonly⁴ 35 to 300°C, preferably 50°C to the boiling point of the diol employed, and especially preferably 80 to 180°C.

The resulting effect will be most potent if the method of the present invention is applied to crude terephthalic acid that has been repeatedly rinsed with acetic acid. The method of the present invention can be applied in this case even when terephthalic acid that has been rinsed

³ [Translator's note: See Item 6(2) of the Amendment section in the original Japanese text.]

⁴ [Translator's note: See Item 6(3) of the Amendment section in the original Japanese text.]

with acetic acid remains wetted with the acetic acid without the complete⁵ removal of the acetic acid.

The method of the present invention is effective on crude terephthalic acid obtained as a result of the so-called "air oxidation method," and its effect is especially dramatic on terephthalic acid having a small particle size; i.e., preferably ten microns or less, and especially five microns or less.

The present invention shall be described in detail below with reference to working examples.

Working Example 1 (illustration of the most typical embodiment)

10 Refined ethylene glycol (water content: 0.1% or less) that is used to manufacture polyethylene terephthalate polymers was charged into a four-neck flask fitted with a water-cooled condenser, a high-efficiency stirrer, and a temperature gauge; and heated to 185°C.

Dried crude terephthalic acid powder (4-CBA content: 0.32%; purity: 99.1% (as determined from the acid value)), which had an average particle size of three microns or less and
15 was obtained by means of *para*-xylene liquid-phase air oxidation using a cobalt catalyst and a *para*-aldehyde co-catalyst, was charged into the flask so that the resulting ethylene glycol/terephthalic acid (weight) ratio was 3.0. The solvent temperature was temporarily lowered to approximately 175°C. The contents were then heated and stirred continuously for ten minutes with the temperature being kept at 180°C, whereupon the heater was removed, and the
20 temperature was lowered to approximately 115°C. The contents were suction-filtered using a magnetic funnel that had been heated in advance to 110°C. The mother liquor was colored. Pressure was applied to the crystals at the top of the funnel to thoroughly drain the mother solution held between the particles. Fresh ethylene glycol was also repeatedly poured on top of the crystals to thoroughly remove the mother liquor in a similar manner (each of the mother
25 liquors was collected separately).

⁵ [Translator's note: The indicated word is a typographical error showing a non-existent Japanese word, but is corrected as indicated in Item 6(4) of the Amendment section in the original Japanese text.]

A portion of the crystal was metered out, charged into a small amount of methanol, and stirred gently. The ethylene glycol held between the crystal particles was replaced with the methanol, the product was then emptied onto the funnel, and the system was suction filtered. More methanol was introduced until all of the ethylene glycol had been replaced thereby, whereupon drying was performed. Calculations were subsequently performed to determine the amount of ethylene glycol contained in the terephthalic acid cake that had been wetted with ethylene glycol as a result of the rinsing and drying processes before being rinsed with methanol. Other portions of the crystal were similarly treated using water, acetone, and acetic acid instead of methanol. In every case, the ethylene glycol content in the terephthalic acid cake that had been wetted with ethylene glycol was 57 to 64% (with regard to the dry terephthalic acid), the purity of the dry terephthalic acid was 100% as determined from its acid value, and the 4-CBA content was 0.07%. An aqueous solution of the crude terephthalic acid as a raw material had a 400 mμ permeability of 56.4% and appeared yellow in color under visual inspection; following the treatment, however, the value improved to 92.3%, and a virtually white, nearly transparent product was obtained. It was accordingly determined that the coloring impurities had also been removed.

It is worth noting that when a common method is used to blend and polymerize ethylene glycol with the raw material and the treated article, the polymer obtained from the raw material will exhibit a dramatically yellow color (Hazen number (color) of the solution: 300 to 500), but the polymer obtained from the treated article will exhibit only minimal coloring (Hazen number (color) of the solution: 50 to 80), thereby confirming that the method of the present invention is effective in removing coloring impurities. Even if a predetermined amount of ethylene glycol has been added to terephthalic acid that has been wetted with ethylene glycol but not subsequently rinsed with methanol, and polymerization has been performed using a treated article that has not been dried, there will still be a marked contrast with the polymer obtained from the raw material, and the coloring will be almost as faint as the polymer obtained from the dry terephthalic acid (Hazen number (color) of the solution: 50 to 150).

Working Example 2 (Effect obtained when the present example is repeatedly treated)

The ethylene glycol-wetted terephthalic acid obtained as described in Working Example 1 was rinsed once more according to the method of Working Example 1. The amount of ethylene glycol used was corrected with regard to the wetted amount. The 4-CBA content was 0.04%, the permeability at 400 mμ was 96.3%, and virtually no coloring could be observed in the polymer.

The same treatment was performed once more; in other words, the treatment of the present invention was performed three times in total. The 4-CBA content was 0.02%, the permeability at 400 mμ was 98.8%, and no further coloring was able to be observed in the polymer.

Working Example 3a (Comparative Example 1)

The method described in Working Example 1 was employed using acetic acid at the boiling point thereof. The treatment was repeatedly performed in the same manner as described in Working Example 2. Based on the results summarized in Table 1, it can be determined that the values obtained for the prior art remained at approximately pre-treatment levels. The data for the previous examples are also provided in the table for reference purposes.

Table 1

	Number of treatment cycles	Purity* (%)	4-CBA content (%)	Permeability at 400 mμ (%)
Prior art (acetic acid)	1	99.6	0.23	71.8
	2	99.7	0.18	78.2
	3	99.7	0.12	83.4
	4	99.7	0.10	91.2
Technique of the present invention (ethylene glycol)	1	100	0.07	92.3
	2	100	0.04	96.8
	3	100	0.02	98.8
	4	100	0.01	99.3
Raw material	0	99.1	0.32	56.4

* Calculated from the acid value

Working Example 3b (Comparative Example 2)

In the present example, methanol and glycerine are used to illustrate that the intended effect is obtained neither with monoalcohols, nor with triols or higher polyalcohols. A treatment was performed in the same manner as described in Working Example 1 in the case of glycerine, and the system was kept for 30 min at 180°C under an elevated pressure in an autoclave in the case of methanol. The results are displayed in Table 2. When methanol was used, a large amount of terephthalic acid dissolved due to esterification, which is also a poor result from an economic perspective, notwithstanding the aspects related to quality described hereunder.

Table 2

	Number of treatment cycles	Purity (%)	4-CBA content (%)	Permeability at 400 mμ (%)
Glycerine	1	99.8	0.15	85.4
	2	99.9	0.12	91.2
Methanol	1	99.4	0.22	76.1
	2	99.4	0.21	82.3

10

Working Example 4 (Effect caused by means of the temperature and treatment time)

The temperature was varied using virtually the same method as described in Working Example 1, and the results are displayed in Table 3. The raw material had a 4-CBA content of 0.29%, and a permeability of 63.2% at 400 mμ.

Table 3

Temperature (°C)	Number of treatment cycles	4-CBA content (%)	Permeability at 400 mμ (%)	Terephthalic acid recovery rate (%)
140	30	0.23	77.7	appx 100
	60	0.21	81.2	appx 100
150	30	0.18	86.5	99.3
	60	0.16	88.7	89.9
160	1	0.28	68.9	appx 100
	10	0.16	90.2	98.5
	30	0.10	91.2	98.1
	60	0.09	92.9	87.5
170	1	0.24	70.0	appx 100
	5	0.15	91.5	99.4
	10	0.11	92.1	97.8
	20	0.08	95.4	97.5
	30	0.05	98.7	94.4
180	1	0.21	75.3	appx 100
	3	0.08	93.4	99.1
	5	0.08	95.7	98.5
	10	0.06	97.6	98.6
	20	0.03	98.6	97.2
	30	0.01	99.1	93.4
	60	<0.01	99.3	84.2
Boiling point	10	<0.03	98.1	86.5
	20	<0.01	99.2	83.4

In other words, at temperatures below 150°C, the permeability at 400 mμ and the 4-CBA content, used in refining methods as indices, went no further than 85% and 0.2% respectively, which are impractical values.

- 5 Although a dramatic refining effect was obtained, esterification caused considerable losses in the mother liquor at or above the vicinity of boiling point as a result of esterification, which was undesirable.

10 It is accordingly preferable to perform the treatment at or above the boiling point, since the time required to dissolve the TPA particles at that temperature will be ten minutes or less, thereby enhancing the refining effect and minimizing loss.

Working Example 5 (Effect caused by means of the filtration temperature)

The filtration temperature was varied for an article treated at 180°C for 20 min in accordance with Working Example 4. The results displayed in Table 4 indicate that a filtration temperature of 50°C or higher is preferred.

5

Table 4

Filtration temperature (°C)	4-CBA content (%)	Permeability at 400 mμ (%)	Terephthalic acid recovery rate (%)
35	0.08	93.4	98.9
48	0.07	93.7	99.3
54	0.04	98.2	96.8
98	0.05	98.7	97.5
135	0.03	98.5	96.3
170	0.03	99.1	93.1

Working Example 6 (Effect caused by means of the amount of ethylene glycol)

10 The amount of ethylene glycol was varied with regard to 100 parts of dry terephthalic acid, and a treatment was performed in virtually the same manner as performed in Working Example 1. The results collectively displayed in Table 5 only indicate that more material was lost with the mother liquor, and that even using 1000 parts or more of the material produced no significant effect.

Table 5

Ethylene glycol/ terephthalic acid	4-CBA content (%)	Permeability at 400 mμ (%)	Terephthalic acid recovery rate (%)
2	0.11	89.7	97.3
3	0.07	92.5	97.1
4	0.07	93.1	92.4
5	0.06	92.9	95.3
8	0.05	93.7	83.4
10	0.04	94.1	81.1
15	0.04	94.8	72.4
20	0.03	94.2	66.6

Working Example 7 (Type of raw material)

The aforementioned method was repeated for crude terephthalic acid (after it had been repeatedly rinsed with acetic acid and water) prepared using a Co-MEK catalyst instead of the Co-*para*-aldehyde catalyst. The filtered mother liquor was refined in virtually the same manner as described in Working Example 1, except that a different color was produced. The treatment was performed at a temperature of 170°C and an ethylene glycol/terephthalic acid ratio of 4.5 for 15 min and with 80°C filtration. The results are displayed in Table 6.

Table 6

	4-CBA content (%)	Permeability at 400 mμ (%)
Raw material terephthalic acid	0.51	31.0
After one treatment	0.11	76.4
After two treatments	0.04	88.7
After three treatments	0.03	89.4

Working Example 8 (Effect caused by means of the size of the raw material particles)

The raw material used in Working Example 7 was filtered and classified into large, medium, and small particle size categories. Each group was treated at a temperature of 175°C

and an ethylene glycol/terephthalic acid ratio of 3.5 for 20 min and with 130°C filtration. In order to illustrate the effect of particle size, the treatment efficiency was determined from the characteristic values before and after the treatment. The results are displayed in Table 7.

$$\text{Treatment efficiency as relates to 4-CBA} = \left(1 - \frac{\text{Content after treatment}}{\text{Content before treatment}} \right) \times 100$$

5
$$\text{Treatment efficiency as relates to permeability at } 400 \text{ m}\mu = \left(1 - \frac{\text{Permeability before treatment}}{\text{Permeability after treatment}} \right) \times 100$$

Table 7

Size	Average particle size (approximate)	Treatment efficiency related to 4-CBA (%)	Treatment efficiency related to permeability (%)
Large	11 microns	39.7	54.7
Medium	5 microns	78.8	65.0
Small	3 microns	80.5	67.0

Working Example 9 (Effect caused by means of the water content)

10 Working Example 7 was performed one more time. Water was forcibly added to the ethylene glycol to adjust the water content thereof. The results displayed in Table 8 indicate that the refining effect deteriorates precipitously if the water content is 5% or greater.

Table 8

Water content (%)	4-CBA content (%)	Permeability at 400 mμ (%)	Terephthalic acid recovery rate (%)
0	0.09	79.4	92.5
1	0.10	88.8	93.1
3	0.08	83.5	92.1
5	0.12	55.2	95.3
7	0.23	66.7	99.4
10	0.30	64.5	99.7

Working Example 10 (Treatment under compression)

Ethylene glycol (water content: 5%) was charged into a 500 mL electromagnetically stirred stainless steel autoclave, and heated to 280°C once the air had been replaced by nitrogen. An ethylene glycol slurry containing terephthalic acid was introduced from a pouring funnel
5 fitted with an equalizer line. The temperature was lowered to 238°C. Heating was stopped and the contents rapidly cooled, after which filtering was performed in the same manner as described in Working Example 1. The 4-CBA content was 0.06%, the permeability at 400 mμ was 96.7%, and the terephthalic acid recovery rate was 88.7%.

The treatment was performed with an ethylene glycol/terephthalic acid ratio of nine. The
10 recovery rate was poorer than that obtained in Working Example 9, but the refining effect was good.

The identical procedure was repeated using acetic acid (at a filtration temperature of 90°C). The 4-CBA content was 0.28, the permeability at 400 mμ was 89.9%, and the terephthalic acid recovery rate was 93.5%. The recovery rate was superior to that obtained with the method of
15 the present invention, but the refining effect was poor.

Nevertheless, the difference between the two becomes more apparent when an attempt is made to polymerize the resulting terephthalic acid with ethylene glycol in accordance with a common method.

The coloring in the polymer obtained by means of the method of the present invention is
20 much less apparent than in the variant treated with acetic acid.

No significant difference could be discerned between the two when a titanium autoclave was used and the ethylene glycol and terephthalic acid were charged and treated at a ratio of 4.2 from the start, thereby suggesting that a profound effect is contributed by the characteristics of the material. In other words, a stainless steel vessel may also be used in the ethylene glycol
25 treatment of the present invention, but conventional acetic acid treatments require the use of an expensive titanium vessel, and therefore the method of the present invention is a far superior technique.

Working Example 11 (Using diols other than ethylene glycol)

Working Example 1 was repeated using alternative diols, with the resulting data being summarized in Table 9. When the treated terephthalic acid had been mixed with the ethylene glycol, heated for several hours, made into a uniform solution, and then polymerized, the softening point of the resulting polymer was lower than when a treatment with ethylene glycol was carried out, and ethylene glycol was still regarded as being the best solvent, probably because trace quantities of high-boiling diols were impossible to remove regardless of how thoroughly the terephthalic acid was rinsed with methanol, water, or the like.

Table 9

	Purity	4-CBA content (%)	Permeability at 400 mμ (%)
Raw material crude terephthalic acid	98.5	0.48	42.4
Ethylene glycol	100	0.68 ⁶	91.9
Diethyl glycol ⁷	100	0.10	89.8
Triethylene glycol	100	0.11	84.4
Propylene glycol	100	0.10	88.8

⁶ [Translator's note: Illegible.]

⁷ [Translator's note: See Item 6(5) of the Amendment section in the original Japanese text.]